

LAW OFFICES

SUGHRUE, MION, ZINN, MACPEAK & SEAS, PLLC

2100 PENNSYLVANIA AVENUE, N.W. WASHINGTON, DC 20037-3213 TELEPHONE (202) 293-7060 FACSIMILE (202) 293-7860 www.sughrue.com

January 31, 2001

BOX PCT

Assistant Commissioner for Patents Washington, D.C. 20231

PCT/JP00/03060 -filed May 12, 2000

Re:

Application of Tetsuo YOSHIDA, Satoshi KITAZAWA, Takashi SAIGO, Masayuki FUKUDA and Shinji

YANO

POLYESTER FILM FOR USE AS AN INK IMAGE RECEIVING BASE FILM AND INK IMAGE

RECEIVING BASE FILM

Our Ref: Q62887

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter I of the Patent Cooperation Treaty:

- ☑ an executed Declaration and Power of Attorney.
- ☑ an English translation of the International Application.
- ☑ Notification Concerning Submission or Transmittal of Priority Document.
- ☑ an executed Assignment and PTO 1595 form.
- ☑ International Search Report and a Form PTO-1449 listing the ISR references.

It is assumed that copies of the International Application, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee is calculated as follows:

Total claims	35	-	20	=	15	X	\$18.00	=	\$270.00
Independent claims	6		3	=	3	x	\$80.00	=	\$240.00
Base Fee		_							\$860.00
Multiple Dependent Claim Fee									\$270.00
TOTAL FILING FEE									\$1640.00
Recordation of Assignment									\$ 40.00
TOTAL FEE									\$1680.00

Checks for the statutory filing fee of \$1640.00 and Assignment recordation fee of \$40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from June 6, 1999, June 30, 1999 and June 30, 1999, based on Japanese Application Nos. No. 11-153539, No. 11-185184 and No. 11-185185, respectively.

Respectfully submitted,

John Callohon Reg. No. 33, 607 Waddell A. Biggart

Registration No. 24,861

WAB/amt

DESCRIPTION

POLYESTER FILM FOR USE AS AN INK IMAGE RECEIVING BASE FILM
AND INK IMAGE RECEIVING BASE FILM

5

10

30

<u>Detailed Description of the Invention</u> Field of the Invention

The present invention relates to a white biaxially oriented polyester film. More specifically, it relates to a white biaxially oriented polyester film for use as a base film for receiving an ink jet printer image, which is excellent in adhesion, gloss, opacifying properties and transportability.

Prior Art

15 Polyester films typified by a polyethylene terephthalate film have been widely used as an image receiving base film. With increasing demand for color printers, new printing system such as ink jet system has been developed. An ink image receiving layer must be formed on the image receiving base film of this printing system as proposed by JP-A 64-36479 and JP-A 1-95091 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). This ink image receiving layer is made from a porous material having excellent ink absorption properties. However, it has poor adhesion to a polyester film used as a base film.

With growing demand for image receiving base films, demand for glossy white films is increasing. It is well known that a white polyester film is obtained by adding a large amount of white inorganic particles such as titanium oxide or calcium carbonate to a polyester. It is also known that a low-density white polyester film is obtained by adding a polyolefin such as polypropylene to a polyester. However, since an olefin is exposed in this film containing a polyolefin, there arise such problems as poor printability,

10

15

low productivity caused by dirty rolls and low gloss. To prevent these problems, methods of producing a laminate film have been proposed (JP-A 7-157581, JP-A 2-26739, etc.). However, when an olefin is added and the obtained white film is bent, wrinkles formed by bending become marked, making the film unsightly.

Problems to be solved by the Invention

It is a first object of the present invention to provide a white polyester film which has a high gloss and excellent opacifying properties and transportability, is free from bending wrinkles and is suitable for use as a base film for receiving an ink jet printer image.

It is a second object of the present invention to provide an adhesive polyester film which has excellent adhesion to an ink image receiving layer, has opacifying properties and is suitable for use as a base film for receiving an ink jet printer image.

Means for solving the Problems

According to studies conducted by the present inventors,

it has been found that the above objects of the present invention are attained by the following (I) white biaxially oriented polyester film for use as a base film for receiving an ink jet printer image and (II) white biaxially oriented polyester laminate film for use as a base film for receiving an ink jet printer image.

- (I) the white biaxially oriented polyester film for use as a base film for receiving an ink jet printer image which satisfies the following requirements (1) to (4).
- (1) The content of titanium oxide particles having an 30 average particle diameter of 0.1 to 0.5 μm in the polyester film is 5 to 20 wt%.
 - (2) The polyester film has an average glossiness of 65 to 95 %.
 - (3) The polyester film has an X-ray diffraction intensity

ratio (F-1/F-2) represented by the following expression (1):

$$0.05 \le (F-1/F-2) \le 0.15$$
 (1)

wherein (F-1) is an X-ray diffraction intensity on a plane (110) parallel to the surface of the film and (F-2) is an X-ray diffraction intensity on a plane (100) parallel to the surface of the film.

- (4) The polyester film has a static friction coefficient of 0.3 to 0.6.
- (II) the white biaxially oriented polyester laminate film for use as a base film for receiving an ink jet printer image which comprises a coating film layer substantially made of the following components (A) to (C) on at least one side of the white biaxially oriented polyester film of the above paragraph (I).
- 15 (A) 50 to 80 wt% of a copolyester having a secondary transition point of 20 to 90°C.
 - (B) 10 to 30 wt% of a water-soluble polymer compound.
 - (C) 3 to 25 wt% of fine particles having an average particle diameter of 20 to 80 nm.
- The present invention will be described in detail hereinafter.

The polyester constituting the polyester film of the present invention is a polyester obtained by polycondensing a diol and a dicarboxylic acid. Typical examples of the dicarboxylic acid include terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, adipic acid, sebacic acid and the like. Typical examples of the diol include ethylene glycol, 1,4-butanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol and the like. Polyethylene terephthalate and polyethylene-2,6-naphthalene dicarboxylate are preferred, and polyethylene terephthalate is particularly preferred. These aromatic polyesters may be a homopolymer or copolymer.

In the case of a copolymer, a copolymerizable component is

15

20

25

a diol component such as diethylene glycol, neopentyl glycol or polyalkylene glycol, or a dicarboxylic acid component such as adipic acid, sebacic acid, phthalic acid, isophthalic acid, 2,7-naphthalenedicarboxylic acid or 5-sodium

sulfoisophthalic acid. The copolymerizable component is used in an amount of 15 mol% or less, preferably 10 mol% or less based on the total of all the dicarboxylic acid components.

In the present invention, a white film is obtained by containing titanium oxide particles in a polyester film. The titanium oxide particles used have an average particle diameter of 0.1 to 0.5 μm , preferably 0.1 to 0.4 μm and are added in an amount of 5 to 20 wt%, preferably 6 to 15 wt%. When the average particle diameter is smaller than 0.1 µm, they agglomerate due to extremely low dispersibility, causing troubles in production process and forming coarse projections on the film. As a result, the obtained film may be inferior in gloss. When the average particle diameter is larger than 0.5 μm , the surface of the film becomes rough with the result of a low gloss. When the amount is smaller than 5 wt%, the obtained film has poor opacifying properties. Therefore, a good product cannot be obtained. When the amount is larger than 20 wt%, the stretchability of the film lowers with the result of a drastic reduction in production efficiency.

Inert particles other than titanium oxide particles can be added to the polyester film of the present invention to improve transportability.

The inert particles other than titanium oxide have an average particle diameter of 0.01 to 5.0 µm and are used in an amount of 0.01 to 0.5 wt%. The inert particles may be either inorganic particles or organic particles. Inorganic particles include silica, alumina, calcium carbonate, barium sulfate and the like. Organic particles include silicone

10

15

20

25

particles and the like. Out of these, silica particles are preferred. When the average particle diameter of the inert particles is smaller than 0.01 μ m, transportability cannot be further improved and when the average particle diameter is larger than 5.0 μ m, glossiness lowers.

The titanium oxide particles and the inert particles other than titanium oxide are surface treated with a fatty acid such as stearic acid or a derivative thereof (surface treating agent) to improve dispersibility. The treatment of titanium oxide particles for improving dispersibility is particularly preferred because the glossiness of the film is improved. Before the titanium oxide particles and the other inert particles are contained in the polyester, it is preferred to carry out the control of particle size or a purification process such as the removal of coarse particles. The industrial means of the purification process include milling means such as a jet mill and ball mill and classification means such as dry and wet centrifugal separators. It is needless to say that these means may be used in combination of two or more or used in different stages. To contain these particles in the polyester, various methods may be used. Typical methods (a) to (c) are given below. (a) The particles are added before the end of an ester exchange reaction or an esterification reaction for the synthesis of a polyester or before the start of a polycondensation reaction.

- (b) The particles are added to a polyester, molten and kneaded.
- (c) A master pellet is produced by adding large amounts of titanium oxide particles and other inert particles in the above methods (a) and (b), and kneaded with a polyester which does not contain these particles such that these particles are contained in a predetermined amount. When the method (a) in which the particles are added at the time of synthesizing

10

15

20

25

a polyester is used, it is preferred to add a slurry prepared by dispersing the titanium oxide particles and the other inert particles in glycol.

The biaxially oriented polyester film of the present invention can be obtained by producing an aromatic polyester containing titanium oxide particles or mixed particles consisting of titanium oxide particles and other inert particles in accordance with the above method, stretching by film formation means which will be described hereinafter and heating. The film forming means and conditions will be described hereinafter. A description is first given of the physical properties of the biaxially oriented polyester film of the present invention.

The biaxially oriented polyester film of the present invention has an average glossiness of 65.0 to 95.0 %, preferably 70 to 90 %. When the average glossiness is lower than 65 %, the biaxially oriented polyester film has a low gloss and is not suitable for use as a base film for receiving an ink jet printer image. When the average glossiness is higher than 95 %, glossiness is fully satisfactory but the surface of the film becomes too flat, whereby a film having poor transportability is obtained.

The biaxially oriented polyester film of the present invention has a thickness of 50 to 250 μm , preferably 60 to 220 μm .

The biaxially oriented polyester film of the present invention has an X-ray diffraction intensity ratio (F-1/F-2) represented by the following expression (1):

$$0.05 \le (F-1/F-2) \le 0.15$$
 (1)

wherein (F-1) is an X-ray diffraction intensity on a plane (110) parallel to the surface of the film and (F-2) is an X-ray diffraction intensity on a plane (100) parallel to the surface of the film.

The above X-ray diffraction intensity ratio (F-1/F-

10

15

20

25

30

2) is in the range of 0.05 to 0.15, preferably 0.07 to 0.12. The X-ray diffraction intensity ratio can be set to the above range by selecting stretching temperatures and draw ratios in longitudinal and transverse directions in the step of film formation from ranges which will be given hereinafter. When the X-ray diffraction intensity ratio is smaller than 0.05, film formation stability lowers and when the X-ray diffraction intensity ratio is larger than 0.15, the average glossiness of the film lowers.

The biaxially oriented polyester film of the present invention has a static friction coefficient of 0.3 to 0.6, preferably 0.31 to 0.57. The static friction coefficient of the film can be set to the above range by blending the above titanium oxide particles and other inert particles into the polyester in the above amounts. When the static friction coefficient of the film is smaller than 0.3, the glossiness of the film lowers and when the static friction coefficient is larger than 0.6, the transportability of the film worsens.

The biaxially oriented polyester film of the present invention has a small thermal shrinkage factor of 2 % or less, preferably 1 % or less when it is heated at 150° C for 30 minutes. When the thermal shrinkage factor is larger than 2 %, the obtained film is not suitable for use as a base film for receiving an ink jet printer image.

Further, it is desired that the biaxially oriented polyester film of the present invention should have a center line average surface roughness (Ra) of 30 to 100 nm, preferably 35 to 80 nm.

In the present invention whose object is to provide a film having a high average glossiness, the average glossiness depends on the molecular orientation of the film in addition to the amounts of the above titanium oxide and other inert particles and the type of the other inert particles. Stated specifically, the molecular orientation rate (MOR) is in the

range of 1.1 to 4.0, preferably 1.2 to 3.8. The molecular orientation (MOR) rate can be set to the above range by selecting stretching conditions which will be described hereinafter, particularly draw rations in longitudinal and transverse directions. Although the relationship between orientation and average glossiness is unknown, it is assumed that the formation of projections by a lubricant added to the film is suppressed by high orientation with the result of a reduction in the surface roughness of the film and an increase in the average glossiness of the base film. A film having an MOR of less than 1.1 has a low average glossiness and large thickness nonuniformity due to low orientation. Therefore, the film is not preferred as a product. A film having an MOR of more than 4.0 has high orientation, thereby deteriorating film formation stability and productivity.

Since the biaxially oriented polyester film of the present invention is used as a base film for receiving an ink jet printer image, it is white and has the above range of average glossiness and an optical density of preferably 0.7 to 1.6. The optical density can be set to the above range by selecting the concentration of titanium oxide particles added. When the optical density is lower than 0.7, the opacifying properties become insufficient and the rear side can be seen disadvantageously. To produce a film having an optical density of more than 1.6, the concentration of titanium oxide particles added must be made higher than necessary, whereby the strength of the film may become low or it may be difficult to form a film.

As described above, the film of the present invention is white and the degree of its whiteness satisfies the following expressions (1) to (3) when lightness defined in CIE 1976 is represented by L* and chroma is represented by C*.

10

30

 $C* \ge 3 \tag{2}$

 $2L* + C* \ge 190$ (3)

(with a proviso that $C^* = \{(a^*)^2 + (b^*)^2\}^{1/2}$).

When lightness (L*) and chroma (C*) do not satisfy any one of the above expressions (1) to (3), the chroma of the film becomes dark, whereby the film is not suitable for use as a base film for receiving an ink jet printer image. To obtain a film having lightness (L*) and chroma (C*) which satisfy the above expressions (1) to (3), the average particle diameter and the concentration of the titanium oxide particles are set to the above ranges, or additives for improving the color of the film are added. For example, the addition of a fluorescent brightener is effective in adjusting the b* value.

According to the present invention, there are provided the above biaxially oriented polyester film and further a white biaxially oriented polyester laminate film (may be simply referred to as "laminate film" hereinafter) for use as a base film for receiving an ink jet printer image which comprises a coating film layer substantially made of the following components (A) to (C) and formed on at least one side of the above film:

- (A) 50 to 80 wt% of a copolyester having a secondary transition point of 20 to 90°C,
- (B) 10 to 30 wt% of a water-soluble polymer compound, and(C) 3 to 25 wt% of fine particles having an average particle diameter of 20 to 80 nm.

The coating film layer formed on the surface of the polyester is substantially made of the above components (A) to (C) and has a thickness of 0.02 to 1 μm , preferably 0.03 to 0.8 μm .

The coating film layer has a surface energy of 54 to 70 mN/m, preferably 55 to 67 mN/m.

A description is subsequently given of the components

15

20

of the coating film layer formed on the surface of the laminate film.

The copolyester (A) of the coating film layer has a secondary transition point (Tg) of 20 to 90°C, preferably 25 to 80°C. When Tg is lower than 20°C, the blocking of the laminate film readily occurs and when Tg is higher than 90°C, the chipping resistance and adhesion of the film lower disadvantageously.

The copolyester (A) is contained in the coating film
layer in an amount of 50 to 80 wt%, preferably 55 to 75 wt%
based on the composition forming the layer.

The copolyester (A) is preferably a copolyester comprising a dicarboxylic acid component having a sulfonate group in an amount of 1 to 16 mol*, preferably 1.4 to 14 mol* based on the total of all the dicarboxylic acid components forming the copolyester.

When the amount of the dicarboxylic acid component having a sulfonate group is smaller than 1 mol* based on the total of all the dicarboxylic acid components forming the copolyester (A), the hydrophilic nature of the copolyester becomes insufficient and when the amount is larger than 16 mol*, the humidity resistance of the coating film layer lowers disadvantageously.

The copolyester (A) is a polyester which comprises a

25 carboxylic acid component such as terephthalic acid,
 isophthalic acid, 2,6-naphthalenedicarboxylic acid,
 hexahydroterephthalic acid, 4,4'-diphenyldicarboxylic acid,
 phenylindanedicarboxylic acid, adipic acid, sebacic acid,
 5-sulfoisophthalic acid, trimellitic acid or

30 dimethylolpropionic acid, a dicarboxylic acid component
 having a sulfonate group such as 5-Na sulfoisophthalic acid,
 5-K sulfoisophthalic acid or 5-K sulfoterephthalic acid, and
 a hydroxy compound component such as ethylene glycol,

diethylene glycol, neopentylene glycol, 1,4-butanediol,

20

25

30

1,6-hexanediol, 1,4-cyclohexanedimethanol, glycerin, trimethylolpropane or bisphenol A adduct with alkylene oxide and is used as an aqueous solution, water dispersion or emulsion.

The water-soluble polymer compound (B) in the coating film layer is contained in an amount of 10 to 30 wt%, preferably 12 to 25 wt% based on the composition forming the layer. At least one selected from the group consisting of a polyvinyl alcohol, polyvinyl pyrrolidone and polyethylene glycol is used as the water-soluble polymer compound (B).

The polyvinyl alcohol as the component (B) preferably has a saponification degree of 75 to 95 mol%. When the saponification degree is lower than 75 mol%, the humidity resistance of the coating film lowers and when the saponification degree is higher than 95 mol%, the adhesion of the coating film to an ink image receiving layer deteriorates disadvantageously. Further, the polyvinyl alcohol is preferably a cation modified polyvinyl alcohol having a saponification degree of 74 to 91 mol% because the adhesion of the resulting coating film to the ink image receiving layer becomes excellent. The polyvinyl pyrrolidone has an K value of 26 to 100. When the K value is smaller than 26, the strength of the coating film becomes low disadvantageously. When the K value is larger than 100, the adhesion of the coating film to the ink image receiving layer deteriorates disadvantageously.

The polyvinyl pyrrolidone preferably has an average molecular weight of 40,000 or more because the chipping resistance of the coating film of the coating film layer becomes excellent.

Copolyethylene glycol obtained by copolymerizing a small amount of propylene glycol in addition to water-soluble polyethylene glycol is used as the polyethylene glycol as the component (B).

10

20

25

30

Out of the above water-soluble polymer compounds (B), the polyvinyl alcohol and polyethylene glycol having a saponification degree of 75 to 95 mol%, the cation modified polyvinyl alcohol having a saponification degree of 74 to 91 mol% and the polyvinyl pyrrolidone having a K value of 26 to 100 are preferred.

The fine particles (C) contained in the coating film layer have an average particle diameter of 20 to 80 nm, preferably 25 to 70 nm. When the average particle diameter of the fine particles (C) is smaller than 20 nm, the blocking of the obtained laminate film readily occurs and when the average particle diameter is larger than 80 nm, the chipping resistance of the laminate film deteriorates.

The fine particles (C) are contained in an amount of 3 to 25 wt%, preferably 5 to 20 wt% based on the composition forming the coating film layer.

The fine particles (C) are organic or inorganic fine particles, as exemplified by calcium carbonate, calcium oxide, aluminum oxide, kaolin, silicon oxide, zinc oxide, crosslinked acrylic resin particles, crosslinked polystyrene particles, melamine resin particles and crosslinked silicone resin particles.

The coating film layer of the present invention is substantially formed from the copolyester (A), the water-soluble polymer compound (B) and the fine particles (C) or from a crosslinked composition comprising the above components (A), (B) and (C) and further a polyfunctional epoxy compound (D).

The adhesion of the coating film layer to the film and further the adhesion of the coating film layer to an ink image receiving layer after printing by means of an ink jet printer are improved by blending and crosslinking this polyfunctional epoxy compound (D).

When the polyfunctional epoxy compound (D) is blended,

10

20

25

30

the amount of the compound (D) is 5 to 20 wt%, preferably 7 to 15 wt% based on the composition of the coating film layer.

The polyfunctional epoxy compound (D) is preferably a compound containing 4 epoxy groups represented by the following formula:

$$\begin{array}{c} \operatorname{CH_2-CH-CH_2} & \operatorname{CH_2-CH-CH_2} \\ \operatorname{N-R-N} & \operatorname{CH_2-CH-CH_2} \\ \end{array}$$

$$\operatorname{CH_2-CH-CH_2} & \operatorname{CH_2-CH-CH_2} \\ \end{array}$$

wherein R is $-CH_2$ $-CH_2$ $-CH_2$ or

$$-$$
CH₂ $-$ C

Another resin such as a melamine resin, antistatic agent, colorant, surfactant and ultraviolet light absorber may be contained in the composition forming the coating film layer in small amounts, in addition to the above components.

A description is subsequently given of the method of forming the white biaxially oriented polyester film of the present invention and the method of forming a coating film layer on the biaxially oriented polyester film.

The polyester film of the present invention can be produced by preparing a polyester composition containing titanium oxide particles and forming a film from the composition by known film forming means per se such as a tenter or inflation method.

Film formation by the tenter method is preferred and the means of film formation is sequential biaxial orientation or simultaneous biaxial orientation. Specifically, sequential biaxial orientation will be described in detail hereinafter. A polyester composition is first dried, molten at a temperature higher than its melting point, extruded from a slit die onto a cooled drum and quenched to produce an

unstretched sheet. This unstretched sheet is heated by rolls or infrared radiation and stretched in a longitudinal direction to obtain a longitudinally stretched film. Longitudinal stretching is preferably carried out making use of the difference of rotation speed between two or more rolls. The longitudinal stretching temperature is preferably higher than the glass transition point (Tg) of the polyester, more preferably 20 to 40°C higher than Tg. The draw ratio, which depends on requirements from application, is preferably 2.5 10 times or more and 4.0 times or less, more preferably 2.8 times or more and 3.9 times or less. When the draw ratio is smaller than 2.5 times, the thickness nonuniformity of the film increases, thereby making it impossible to obtain a satisfactory film. When the draw ratio is larger than 4.0 15 times, the rupture of the film readily occurs during film formation. The longitudinally stretched film is subsequently stretched in a transverse direction and heat set and optionally thermally relaxed to obtain a biaxially oriented film. These treatments are carried out on line 20 while the film is caused to run. Transverse stretching is first carried out at a temperature 20°C higher than the glass transition point (Tg) of the polyester and then by increasing the temperature to a temperature (120 to 30)°C lower than the melting point (Tm) of the polyester. The stretching 25 start temperature is preferably (Tg + 40)°C or less. The maximum stretching temperature is preferably a temperature (100 to 40)°C lower than Tm. Increasing the temperature in the step of stretching the film in a transverse direction may be carried out continuously or stepwise (sequentially). 30 Generally speaking, the temperature is increased sequentially. For example, the transverse stretching zone of the tenter is divided into a plurality of sections in the running direction of the film and a heating medium having

a predetermined temperature is caused to flow into each zone

10

15

20

25

30

to increase the temperature. When the transverse stretching start temperature is too low, the rupture of the film occurs disadvantageously. When the maximum stretching temperature is lower than $(Tm - 120)^{\circ}C$, the thermal shrinkage of the film becomes large and uniformity in the physical properties of the film in a width direction lowers disadvantageously. When the maximum stretching temperature is higher than $(Tm - 30)^{\circ}C$, the film becomes soft and ruptures by disturbance or the like disadvantageously. The transverse draw ratio is preferably 2.5 times or more and 4.0 times or less, more preferably 2.8 times or more and 3.9 times or less. Below 2.5 times, nonuniformity in the thickness of the film increases, thereby making it impossible to obtain a satisfactory film. Above 4.0 times, the rupture of the film readily occurs during film formation.

In the present invention, the coating film layer made of the above components is formed on at least one side of the white polyester film. For example, an aqueous solution containing components for forming the coating film layer is applied to a stretchable polyester film, dried and stretched and optionally heated to form a coating film layer on the The solid content of the aqueous solution polyester film. is generally 30 wt% or less, preferably 10 wt% or less. above stretchable polyester film is an unstretched polyester film, uniaxially stretched polyester film or biaxially oriented polyester film. Out of these, a uniaxially stretched polyester film which is stretched in an extrusion (longitudinal) direction of the film is particularly preferred. When an aqueous solution is to be applied to the polyester film, it is not preferred to carry out a general coating step, that is, apply the aqueous solution to the biaxially oriented heat set polyester film, separate from the film production step, because dust and the like are easily contained in the film. Coating in a clean atmosphere, that

30

is, coating in the film production step is preferred from the above point of view. The adhesion of the coating film to the polyester film is further improved by this coating. Any known coating method can be employed. For example, roll coating, gravure coating, roll brushing, spray coating, air knife coating, impregnation and curtain coating may be used alone or in combination. The amount of coating is 0.5 to 20 g, preferably 1 to 10 g per 1 m² of the running film. The aqueous solution is preferably a water dispersion or emulsion.

Specific examples (a) to (d) of the laminate film of the present invention are given below. In the following description, the expression "white polyester film" means a biaxially oriented film.

- (a) A polyester laminate film for use as a base film for receiving an ink image, wherein a coating film layer is formed on at least one side of the white polyester film, the coating film layer substantially comprising (A) 50 to 80 wt% of a copolyester having a secondary transition point of 20 to 90°C
- and containing a dicarboxylic acid component having a sulfonate group in an amount of 1 to 16 mol% based on the total of all the dicarboxylic acid components forming the copolyester, (B) 10 to 30 wt% of a water-soluble polymer compound and (C) 3 to 25 wt% of fine particles having an average particle diameter of 20 to 80 nm, and having a surface

energy of 54 to 70 mN/m.

(b) A polyester laminate film for use as a base film for receiving an ink image, wherein a coating film layer is formed on at least one side of the white polyester film, the coating film layer substantially comprising (A) 30 to 80 wt% of an aqueous binder, (B) 10 to 40 wt% of a water-soluble polymer, (C) 3 to 25 wt% of fine particles having an average particle diameter of 20 to 80 nm and (D) 5 to 20 wt% of a polyfunctional epoxy compound crosslinking agent as essential ingredients

10

15

20

30

and having a surface energy of 50 to 70 mN/m.

- (c) A white polyester laminate film for use as a base film for receiving an ink image, comprising a polyester film which (A) a copolyester, (B) polyethylene glycol and (C) a coating layer formed on fine particles as essential ingredients are formed on at least one side of the white polyester film, the polyester film containing 5 to 20 wt% of titanium oxide having an average particle diameter of 0.1 to 0.2 μ m and 0.01 to 0.5 wt% of inert particles other than titanium oxide having an average particle diameter of 0.01 to 5.0 μ m and having an average glossiness of 80.5 to 95 % and a static friction coefficient of 0.30 to 0.50.
- (d) A white polyester laminate film comprising a polyester film which (A) a copolyester, (B) polyethylene glycol and (C) a coating layer formed on fine particles as essential ingredients are formed on at least one side of the white polyester film, the polyester film containing 5 to 20 wt% of titanium oxide having an average particle diameter of 0.2 to 0.5 μ m and 0.01 to 0.5 wt% of inert particles other than titanium oxide having an average particle diameter of 0.01 to 5.0 μ m, and having an average glossiness of 65 to 80 % and an X-ray diffraction intensity ratio (F-1/F-2) which satisfies the following expression (1):

$$0.05 \le (F-1/F-2) \le 0.15 \tag{1}$$

25 wherein (F-1) is an X-ray diffraction intensity on a plane $(\overline{110})$ parallel to the surface of the film and (F-2) is an X-ray diffraction intensity on a plane (100) parallel to the surface of the film.

Effects of the Invention

According to the present invention, there can be provided a white polyester film useful as a base film for receiving an ink jet printer image which has a high gloss and excellent opacifying properties and transportability and is free from bending wrinkles.

Examples

5

20

25

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting. The characteristic properties of the film were measured in accordance with the following methods.

(1) secondary transition point

This is measured with the Thermal Analyst 2000

10 differential calorimeter of DuPont Co., Ltd. at a temperature increasing rate of 20°C/min.

(2) intrinsic viscosity

This is measured for viscosity of a solution in an orthochlorophenol solvent at 35°C.

15 (3)-(a) adhesion before printing

An aqueous slurry prepared by mixing 70 wt% of spherical silica (average particle diameter of 18 µm, average pore diameter of 200 Å, average pore volume of 1.5 cc/g) and 30 wt% of a polyvinyl alcohol (PVA117 of Kuraray Co., Ltd.) is applied to the coating film surface of a polyester film to a dry thickness of 20 µm, and Scotch tape (No. 600 of 3M Limited) having a width of 12.7 mm and a length of 150 mm is affixed to the coating film such that air bubbles are not contained therein, bonded to the coating film by rolling with a manual roll specified in JIS·C2701 (1975) and cut to the width of the tape. By removing the Scotch tape from the thus prepared sample, the peeling of the ink image receiving layer from the polyester film is observed to evaluate adhesion as follows.

- 30 A: Peeling is not observed at all and adhesion is excellent.

 B: The peeling of a foreign matter portion is slightly observed.
 - C: Peeling is markedly observed.
 - (3)-(b) adhesion after printing

15

25

30

An aqueous slurry prepared by mixing 70 wt% of spherical silica (average particle diameter of 18 µm, average pore diameter of 200 Å, average pore volume of 1.5 cc/g) and 30 wt% of a polyvinyl alcohol (PVA117 of Kuraray Co., Ltd.) is applied to the coating film surface of a polyester film to a dry thickness of 20 µm and printed with a PC image as input data taken by a digital camera or the like by an ink jet printer (PM-750C of Epson Co., Ltd.), and Scotch tape (No. 600 of 3M Limited) having a width of 12.7 mm and a length of 150 mm is affixed to this printed coating film such that air bubbles are not contained therein, bonded to the coating film by rolling with a manual roll specified in JIS·C2701 (1975) and cut to the width of the tape. By removing the Scotch tape from the thus prepared sample, the peeling of the ink image receiving layer from the polyester film is observed to evaluate adhesion as follows.

A: Peeling is not observed at all and adhesion is excellent B: The peeling of a foreign matter portion is slightly observed.

20 C: Peeling is markedly observed

(4) friction coefficient

The front side and rear side of the film are joined together and a load of 1 kg is applied to the film to measure the static friction coefficient of the film with the slip measuring instrument of Toyo Tester Co., Ltd. in accordance with ASTM·D1894-63. When the friction coefficient is larger than 0.6, the transportability of the film becomes unsatisfactory.

(5) antiblock properties

Two films cut to a width of 50 mm are placed one upon the other and treated under a load of 50 kg/cm^2 at a temperature of 40° C and a relative humidity of 50 % for 17 hours to measure the peel strength (g/50 mm) of a loaded portion with a tensile tester. The peel strength is evaluated as follows.

peel strength \leq 10 g/50 mm: excellent

10 g/50 mm < peel strength \leq 30 g/50 mm: good

30 g/50 mm < peel strength: poor

- (6) surface energy
- The critical surface tension γc measured in accordance with W. A. Zisman: "Contact Augle, Wettability and Adhesion", Am. Chem. Soc., (1964) is taken as surface energy.
 - (7) water dispersibility

A coating agent is diluted with water to prepare a 0.2

10 wt% water dispersion so as to measure the light transmittance of the water dispersion by the double-beam spectrophotometer (Model 228A) of Hitachi, Ltd. using a quartz cell. The water dispersibility of the coating agent is evaluated from the measurement result as follows.

15 transmittance ≥ 50 %: excellent

50 % > transmittance ≥ 30 %: good

30 % > transmittance: poor

(8) humidity resistance

Peel strength (g/50 mm) is measured in the same manner as evaluation for the evaluation of antiblock properties except that the treatment conditions are changed to 60°C x 70 %RH x 17 hours. Humidity resistance is evaluated from the measurement result as follows.

peel strength \leq 10 g/50 mm: excellent

- 25 10 g/50 mm < peel strength \leq 30 g/50 mm: good 30 g/50 mm \leq peel strength: poor
 - (9) average glossiness (Gs)

This is measured with the GM-3D glossimeter of Murakami Shikisai Gijutsu Kenkyusho in accordance with JIS Z 8741-1962.

- The measurement angle is 60°, the number n of times of measurement is 5, and the means value of measurement data is taken as average glossiness (Gs).
 - (10) light transmittance

This is measured with the HR-100 haze meter of Murakami

15

25

Shikisai Gijutsu Kenkyusho in accordance with ASTM·D1003. (11) thermal shrinkage factor

The shrinkage factor of a polyester film after it is heated at 150°C for 30 minutes is measured at a distance between gage marks of 30 cm.

(12) center line average roughness (Ra)

When a chart is drawn by the SE-3FAT high-precision surface roughness meter of Kosaka Kenkyusho Co., Ltd. in accordance with JIS B0601 at a needle radius of 2 μ m, a load of 30 mg, a magnification of 50,000% and a cut-off of 0.08 mm, a measurement length L portion is extracted from the surface roughness curve in a center line direction, and the center line of the extracted portion is plotted as an X axis and the direction of the longitudinal draw ratio is plotted as a Y axis to express the roughness curve by Y = f(x), a value given by the following expression is expressed in unit of nm.

$$Ra = \frac{1}{L} \int_0^L |f(x)| dx$$

This measurement is made 4 times at a standard length of 1.25 mm and the mean value of the measurement data is taken as center line average roughness.

(13) sharpness

An image taken by a digital camera or the like is input into a personal computer and printed on a polyester film having an ink image receiving layer by an ink jet printer (PM-750C of Epson Co., Ltd.) to observe the clearness of the printed matter by the eye and evaluated as follows.

A: printed image is very clear excellent

B: printed image is clear good

30 C: printed image is unclear poor

(14) molecular orientation rate (MOR)

The plot of an oriented oval is obtained using the

25

30

MOA-2001A molecular orientation meter of Oji Paper Co., Ltd. and the ratio of long axis to short axis calculated based on this plot is taken as molecular orientation rate (MOR). (15) transportability

- 100 films are piled up on the paper feed tray of the PM-700C ink jet printer of Epson Co., Ltd. and printed in a continuous paper feed mode to judge the transportability of the films based on the following criteria.
 - O: 2 or less films fail to be fed and carried
- 10 \triangle : 3 to 5 films fail to be fed and carried
 - imes: more than 5 films fail to be fed and carried
 - (16) opacifying properties

A 5 mm wide and 5 cm long line is drawn on one side of the film with a black oil magic marker and observed from the other side of the film to judge the opacifying properties of the film based on the following criteria.

- O: black line cannot be seen at all.
- \triangle : black line is slightly seen.
- X: black line can be seen clearly.
- 20 (17) X-ray diffraction intensity ratio

The ratio (f(100)/f(1-10)) of X-ray diffraction intensity (f(100)) on a plane (100) parallel to the surface of the film to X-ray diffraction intensity (f(1-10)) on a plane (1-10) parallel to the surface of the film is measured by a multiplex peel separation method using a Pseudo Voight peel model using CuK- α as an X-ray source, at a divergent slit of $1/2^{\circ}$, a diffusion slit of $1/2^{\circ}$, a receiving slit of 0.15 mm and a scanning speed of $1,000^{\circ}$ /min. The area of the diffraction peak of each crystal plane is obtained and taken as X-ray diffraction intensity. A reflection peak derived from a pigment such as titanium oxide is located near f(100) and the area is obtained by excluding this.

(18) optical density

Films are piled up to a thickness of about 100 μm and

10

15

20

25

30

measured with an optical densimeter (X-Rite 310TR). Thickness and optical density are plotted to obtain optical density when the thickness of the laminate is 100 μ m. (19) L*/a*/b* values

A film is placed on a white standard plate having three stimulus values, Y = 94.95, X = 93.63 and Z = 112.32 and measured with the SZ- \sum 90 color difference meter of Nippon Denshoko Kogyo Co., Ltd. The L* value, a* value and b* value are based on L*/a*/b* color specification system defined by CIE1976.

Example I and Comparative Example I

Anatase titanium oxide particles and other inert particles shown in Table 1 were added to polyethylene terephthalate, melt extruded at 280°C and solidified by cooling to obtain an unstretched film. This unstretched film was stretched in a longitudinal direction and then a transverse direction under conditions shown in Table 1 and heat set to obtain a 100 µm thick white film. Right after stretching in the longitudinal direction, the white film was coated with an aqueous solution composed of 65 wt% of a copolyester (Tg = 30°C) consisting of terephthalic acid (60 mol%), isophthalic acid (37 mol%) and 5-Na sulfoisophthalic acid (3 mol%) as acid components and ethylene glycol(40 mol%), neopentyl glycol (40 mol%) and bisphenol A adduct with ethylene oxide (20 mol%) as glycol components, 16 wt% of polyethylene oxide having a molecular weight of 1,000, 10 wt% of crosslinked acrylic resin particles having an average particle diameter of 40 nm and 9 wt% of polyoxyethylene nonylphenyl ether, and having a solid content of 4 wt% by a roll coater. The characteristic properties of this laminate film are shown in Table 1.

Table 1

	titanium	oxide	lubrica	nt (second c	omponent)	titanium oxide ubricant (second component) static friction	average	Ra
						coefficient	glossiness	
	particle am	amount	type	particle	amount)	
-	diameter			diameter				
	mr	wt%		mrd	wt%			mu
欧. I-(1)	0.15	10	silica	0.03	0.05	0.40	88	4.1
Ex. I-(2)	0.15	20	silica	0.03	0.05	0.35	82	44
Ex. I-(3)	0.15	10	silica	0.03	0.05	0.38	92	38
Ex. I-(4)	0.15	10	silica	0.03	0.05	0.44	83	44
Ex. I-(5)	0.15	ស	silica	1.50	0.50	0.31	81	46
C.既.I-(1)	0:30	20	silica	0.03	0.05	0.38	09	89
C.Ex. I-(2)	0.15	10	none	1	1	0.62	93	32
C.Ex. I-(3)	0.15	10	silica	5.50	0.01	0.29	63	99
C.Ex. I-(4)	0.15	ဗ	silica	4.00	0.30	0.33	81	53
C.Ex. I-(5)	0.15	10	silica	0.03	0.05	0.40	79	48

Ex.: Example C.Ex.: Comparative Example

Table 1 (continued)

	longitudinal		transverse	stretching	MOR	opacifying	stretching transverse stretching MOR opacifying transportability
	condit	itions	condi	conditions		properties	
ت	temperature	draw ratio	temperature	temperature draw ratio			· - · · ·
	ວ.		ວຸ				
	100	3.0	120	3.3	2.5	0	0
	100	3.0	120	3.3	2.5	0	0
	110	3.0	120	3.5	3.8	0	0
	110	3.0	120	3.1	1.2	0	0
	100	3.0	120	3.3	2.5	0	0
	100	3.0	120	3.3	2.5	0	0
	100	3.0	120	3.3	2.5	0	×
	100	3.0	120	3.3	2.5	0	0
	100	3.0	120	3.3	2.5	abla	0
C.Ex. I-(5)	110	3.0	120	3.0	1.0	0	0

Example II and Comparative Example II

Anatase titanium oxide particles shown in Table 2 were added to polyethylene terephthalate, melt extruded at 280°C and solidified by cooling to obtain an unstretched film. This unstretched film was stretched in a longitudinal 5 direction and then a transverse direction under conditions shown in Table 2 and heat set to obtain a 100 µm thick white film. Right after stretching in the longitudinal direction. the white film was coated with an aqueous solution composed 10 of 65 wt% of a copolyester (Tg = 30°C) consisting of terephthalic acid (60 mol%), isophthalic acid (37 mol%) and 5-Na sulfoisophthalic acid (3 mol%) as acid components and ethylene glycol(40 mol%), neopentyl glycol (40 mol%) and bisphenol A adduct with ethylene oxide (20 mol%) as glycol 15 components, 16 wt% of polyethylene oxide having a molecular weight of 1,000, 10 wt% of crosslinked acrylic resin particles having an average particle diameter of 40 nm and 9 wt% of polyoxyethylene nonylphenyl ether, and having a solid content of 4 wt% by a roll coater. The characteristic 20 properties of this laminate film are shown in Table 2.

Table 2

	Trantal	titanium oxide	longitudinal	udinal	transverse	transverse stretching
			stretching	stretching conditions	conditions	tions
<u>D</u>	article	amount	temperature	particle amount temperature draw ratio temperature draw ratio	temperature	draw ratio
פֿי	diameter	Wt%	ပ		ນຸ	
	mrd					
Ex. II-(1)	0.3	12	100	3.0	120	3.3
Ex.II-(2)	0.4	20	100	3.0	120	3.3
Ex.II-(3)	0.3	12	110	3.0	120	3.5
Ex.II-(4)	0.3	12	110	3.0	120	3.1
Ex.II-(5)	0.4	5	100	3.0	120	3.3
C.Ex.II-(1)	0.3	20	100	3.0	120	3.3
C.Ex.II-(2)	0.08	20	100	3.0	120	3.3
C.Ex.II-(3)	0.3	20	110	3.0	120	3.0

Ex.: Example C.Ex.: Comparative Example

Table 2 (continued)

	X-ray diffraction	average	static	optical	*1	*ပ	$2L^*+C^*$	optical L* C* 2L*+C*transport
	intensity ratio	glossiness	friction	density				ability
		:	coefficient					ľ
Ex. II-(1)	0.08	92	0.48	0.8	93	9	192	C
Ex. II-(2)	0.08	89	0.44	1.3	94	9	:) O
Ex.II-(3)	0.05	79	0.51	1.0	93	9	192	0
Ex. II-(4)	0.15	99	0.43	6.0	93	9	192	О
Ex.II-(5)	0.08	83	0.53	0.7	95	5	195) O
C.欧.II-(1)	0.08	19	0.38	1.2	93	က	189	C
C.Ex.II-(2)	0.1	98	0.63	1.1	94	÷	202	×
C.Ex.II-(3)	0.2	63	0.41	1.5	93	6	195	C

15

Example III and Comparative Example III

Anatase titanium oxide particles and other inert particles shown in Table 3 were added to polyethylene terephthalate, melt extruded at 280°C and solidified by cooling to obtain an unstretched film. This unstretched film was stretched in a longitudinal direction and then a transverse direction under conditions shown in Table 3 and heat set to obtain a 100 µm thick white film. Right after stretching in the longitudinal direction, the white film was coated with an aqueous solution composed of 65 wt% of a copolyester (Tg = 30°C) consisting of terephthalic acid (60 mol%), isophthalic acid (37 mol%) and 5-Na sulfoisophthalic acid (3 mol%) as acid components and ethylene glycol(40 mol%), neopentyl glycol (40 mol%) and bisphenol A adduct with ethylene oxide (20 mol%) as glycol components, 16 wt% of polyethylene oxide having a molecular weight of 1,000, 10 wt% of crosslinked acrylic resin particles having an average particle diameter of 40 nm and 9 wt% of polyoxyethylene nonylphenyl ether, and having a solid content of 4 wt% by a roll coater. The characteristic properties of this 20 laminate film are shown in Table 3.

Table 3

	titanium oxide	n oxide	lubr	lubricant (second	cond	longitudinal	udinal	transverse	transverse stretching
			Ö	component)		stretching conditions	conditions	conditions	tions
	particle amount	amount	type	particle	amount	temperature	draw ratio	The particle amount temperature draw ratio temperature draw ratio	draw ratio
	diameter	wt%		diameter		ບຸ		ນຸ	
	mrd			mrl	wt%				
Ex. III-(1)	0.3	10	silica	0.03	0.05	100	3.0	120	3.3
Ex. III-(2)	0.3	20	silica	0.03	0.05	100	3.0	120	3.3
Ex. III-(3)	0.3	10	silica	0.03	0.05	110	3.0	120	3.5
Ex. III-(4)	0.3	10	silica	0.03	0.05	110	3.0	120	3.1
Ex. III-(5)	0.3		silica	1.50	0.50	100	3.0	120	3.3
C.Ex. III-(1)	0.5	20	silica	0.03	0.05	100	3.0	120	3.3
C.Ex.III-(2)	0.3	20	none			100	3.0	120	3.3
C.Ex.III-(3)	0.3	20	silica	0.03	0.05	110	3.0	120	3.0

Ex.: Example C.Ex.: Comparative Example

Table 3 (continued)

'' '	\Box							
transpor ability	0	0	0	0	0	0	×	0
2L*+C*	200			200	195	189		195
*ల	14	14	14	14	5	က	14	6
* ₋	93	94	93		95	93	94 14	93
optical L* C* 2L*+C*transport density	0.8	1.3	1.0	6.0	0.7	1.2	1.1	1.5
average glossiness	75	70	78	65	89	09	78	63
X-ray diffraction average optical intensity ratio glossiness density	0.10	0.10	0.05	0.15	0.10	0.10	0.10	0.20
	Ex. III-(1)	Ex. III-(2)	Ex. III-(3)	Ex.III-(4)	Ex. III-(5)	C.Ex.III-(1)	C.Ex.III-(2)	C.Ex.III-(3)

Example IV-1

5

10

15

20

25

A polyester (intrinsic viscosity of 0.62) composed of a terephthalic acid component and an ethylene glycol component was melt extruded onto a rotary cooling drum maintained at 20°C to obtain an unstretched film which was then stretched to 3.6 times in a mechanical axis direction and coated with an aqueous solution composed of 65 wt% of a copolyester (Tg = 30°C, to be simply referred to as "E" hereinafter)) which consisted of terephthalic acid (60 mol%). isophthalic acid (36 mol%) and 5-Na sulfoisophthalic acid (4 mol%) as acid components and ethylene glycol(60 mol%) and neopentyl glycol (40 mol%) as glycol components, 16 wt% of a polyvinyl alcohol having a saponification degree of 86 to 89 mol%, 10 wt% of crosslinked acrylic resin particles having an average particle diameter of 40 nm and 9 wt% of polyoxyethylene lauryl ether, and having a solid content of 4 wt% by a roll coater.

The longitudinally stretched film coated with the aqueous solution was stretched to 4 times in a transverse direction while it was dried, and then heat set at 230°C to obtain a 100 μ m thick biaxially oriented film.

The film had a coating film thickness of 0.03 μ m, a center line average surface roughness of 15 nm, a surface energy of 60 mN/m and a thermal shrinkage factor in a longitudinal direction of 0.9 % and in a transverse direction of 0.2 %. The characteristic properties of this laminate film are shown in Table 4.

Comparative Example IV-(1)

The characteristic properties of a biaxially oriented polyester film obtained in the same manner as in Example IV-(1) except that the aqueous solution was not coated are shown in Table 4.

Examples IV-(2) to IV-(12)

Biaxially oriented polyester films were obtained in the

same manner as in Example IV-(1) except that the type and amount of the coating agent was changed as shown in Table 4. The characteristic properties of this laminate film are shown in Table 4.

Table 4

							adherion	anreage
		Com	composition of co	coating film	layer		adileston	anerciv
•	(A) copolvester	vester	(B) water-soluble polymer	le polymer	(C) fine	particles		(mN/m)
	type	wt%	type	wt%	type	wt%		(/ \ \
	(note 1)		(note 2)		(note 3)			
	1 222	7.5	d	16	M	10	A	09
EX. IV (1)	a p	20	<u>a</u>	11	M	10	A	57
EX. IV=(2)	a r	0 4		16	M	10	A	58
EX. IV=(3)	리	20 7	ם וכ	16	Σ	10	Ą	56
EX. IV-(4)	FI I	00	4 0	16	Σ	10	A	60
(C)-AT-XI	±1 [000	4 F	16	Σ	10	A	56
EX. IV-(6)	***	2 ;	4 F	10	ž	10	A	63
Ex. IV-(7)	ŭ	09	Σi I	7.7	: 2	10	A	64
Ex. IV-(8)	Ħ	65	- 1	OT	E 2	0 -	A	64
Ex. IV-(9)	ы	65	Ω	OT TO	E	OT		O LI
Ex. IV-(10)	М	65	M	16	Σ	10	A	000
Ex TV-(11)	F	65	×	16	M	10	А	57
Fx. TV-(12)	i M	68	Q	16	Z	10	A	59
C EX. TV-(1)	1					7	ບ	47
1								

Ex.: Example C.Ex.: Comparative Example

As is obvious from the results shown in Table 4, the polyester film for an ink jet printer image receiving layer of the present invention has excellent adhesion.

In Table 4, the types E and F of copolyester (note 1) are the following copolymers.

E: copolymer (Tg = 30°C) consisting of terephthalic acid (60 mol%), isophthalic acid (36 mol%) and 5-Na sulfoisophthalic acid (4 mol%)/ethylene glycol (60 mol%) and neopentyl glycol (40 mol%)

10 F: copolymer (Tg = 42°C) consisting of 2,6naphthalenedicarboxylic acid (20 mol%), isophthalic acid (76
mol%) and 5-K sulfoterephthalic acid (4 mol%)/ethylene
glycol (50 mol%) and neopentyl glycol (50 mol%)

In Table 4, the types P, Q, R, T, U, W and X (note 2)

of water-soluble polymer compound are the following compounds.

P: polyvinyl alcohol having a saponification degree of 86 to 89 mol%

Q: polyvinyl alcohol having a saponification degree of 76

20 to 82 mol%

R: polyvinyl alcohol having a saponification degree of 91 to 94 mol%

T: polyvinyl pyrrolidone having a K value of 26 to 23 and an average molecular weight of 40,000

U: polyvinyl pyrrolidone having a K value of 90 to 100 and an average molecular weight of 1,200,000

W: cation modified polyvinyl alcohol having a saponification degree of 74 to 80 mol%

X: cation modified polyvinyl alcohol having a saponification
30 degree of 86 to 91 mol%

In Table 4, the types M and N (note 3) of fine particles are the following compounds.

M: crosslinked acrylic resin particles having an average particle diameter of 40 nm

10

N: colloidal silica particles having an average particle diameter of $80\ \mathrm{nm}$

Examples IV-(13) to IV-(16) and Comparative Examples IV-(2) and IV-(3)

Biaxially oriented polyester films were obtained in the same manner as in Example IV-(1) except that the type of copolyester (A) of the coating film layer was changed as shown in Table 5 and Table 6 and copolyesters having different Tg's were used. The characteristic properties of the obtained laminate films are shown in Table 5.

Table 5

	type of (A) (note 4)	Tg of (A) (°C)	antiblock properties	adhesion
Ex.IV-(13)	G	24	good	A
Ex.IV-(14)	H	45	excellent	A
Ex.IV-(15)	I	65	excellent	A
Ex.IV-(16)	J	79	excellent	В
C.Ex.IV-(2)	K	17	poor	A
C.Ex.IV-(3)	L	98	excellent	С

Ex.: Example C.Ex.: Comparative Example

Table 6

4	16 80	16 80	16 80 4	30 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4			
,		1 1 1			16 8(80 80 2	16 80 80 80 5 60
	36	36	36 60	36 60	36 60 4 4	36 60 4 4	36 60 4 70 10
	70	70	70 24	24 6	70 24 6	70 24 6 60 3	70 24 6
	46	46 40 10	46 40 10	40 10	46 40 10 4	46 40 10 4 60	46 40 10 4 60 60
	90	30	30	30	60 30 4	60 30 4 4 5	60 30 4 5 5
	halic acid halic acid	halic acid halic acid edicarboxylic acid	halic acid halic acid edicarboxylic acid sophthalic aid	halic acid halic acid edicarboxylic acid sophthalic aid	halic acid halic acid edicarboxylic acid sophthalic acid ophthalic acid	halic acid halic acid edicarboxylic acid sophthalic aid ophthalic acid ne glycol	halic acid halic acid edicarboxylic acid sophthalic aid ne glycol ene glycol tranedlol
	terephth isophtha	terephth isophtha 2,6-naphthalenec	terephtha isophtha 2,6-naphthalened 5-Na sulfois	terephtha isophtha 2,6-naphthalened 5-Na sulfoiso 5-K sulfoiso	isophtha isophtha 2,6-naphthalened 5-Na sulfoiso 5-K sulfoiso ethylen	terephtha isophtha 2,6-naphthalened 5-Na sulfoiso 5-K sulfoiso ethylened	terephthalished 2,6-naphthalened 5-Na sulfoiso 5-K sulfoiso ethylen diethyle
46	40	30 40 lic acid 10	30 40 10 4	30 40 10 4 4	30 40 10 4 4 5 60	30 40 10 4 4 5 60	30 40 10 4 4 60 5 60 3 2 42 2

As is obvious from the results shown in Table 5, the polyester film for an ink jet printer image receiving of the present invention has excellent antiblock properties and adhesion.

Examples IV-(17) to IV-(21) and Comparative Examples IV-(4) and IV-(5)

Biaxially oriented polyester films were obtained in the same manner as in Example IV-(1) except that the proportion of the dicarboxylic acid component containing a sulfonate group of the copolyester (A) was changed as shown in Table 7. The characteristic properties of the obtained laminate films are shown in Table 7.

C.Ex.: Comparative Example

Ex.: Example

Table 7

	proportions of dic	of dicarboxylic acid components	omponents	water	humidity
	of copoly	copolyester (A) (mol %)		dispersibility	resistance
	5-Na sulfoisophthalic acid	acid terephthalic acid isophthalic acid	isophthalic acid		
Ex.IV-(17)	r-I	09	39	good	excellent
Ex.IV-(18)	2	09	38	excellent	excellent
Ex.IV-(19)	9	09	34	excellent	excellent
Ex.IV-(20)	12	09	28	excellent	excellent
Ex.IV-(21)	16	09	24	excellent	good
C.Ex. IV-(4)	0	09	40	poor	excellent
C.Ex.IV-(5)	20	09	20	excellent	poor

As is obvious from the results shown in Table 7, the coating agent of the present invention is excellent in water dispensability and the polyester film for an ink jet printer image receiving of the present invention is excellent in humidity resistance.

Examples IV-(22) to IV-(24) and Comparative Examples IV-(6) to IV-(9)

Biaxially oriented polyester films were obtained in the same manner as in Example IV-(1) except that the ratio of the copolyester (A), the water-soluble polymer (B) and fine particles (C) was changed as shown in Table 8. The characteristic properties of the obtained laminate films are shown in Table 8.

C.Ex.: Comparative Example

Ex.: Example

Table 8

)	composit	composition of coating film layer	ating f	ilm layer		adhesion	friction	surface
	(A) copolyester	yester	(B) water-	soluble	(B) water-soluble (C) fine particles	ticles		coefficient	energy
			polymer	er					(m/Nm)
	type	wt%	type	wt%	type	wt%			
Ex.IV-(22)	H	55	P	26	X	10	A	0.32	65
Ex.IV-(23)	Н	61	P	20	М	10	A	0.33	62
Ex. IV-(24)	Н	70	P	11	M	10	A	0.38	58
C.Ex.IV-(6)	Н	20	P	40	M	10	В	69.0	7.0
C.Ex.IV-(7)	Н	61	P	2	М	10	၁	0.32	5.1
C.Ex.IV-(8)	Н	31	Ъ	20	M	10	C	0.62	7.0
C.Ex.IV-(9)	н	74	Ъ	7	М	10	ນ	0.34	53

As is obvious from the results shown in Table 8, the polyester film for receiving an ink jet printer image of the present invention is excellent in adhesion and transportability.

5 Examples IV-(25) and IV-(26) and Comparative Examples IV-(10) and IV-(11)

Biaxially oriented polyester films were obtained in the same manner as in Example IV-(1) except that the particle diameter of the fine particles (C) was changed as shown in Table 9. The characteristic properties of the obtained laminate films are shown in Table 9.

Table 9

	average particle diameter of fine particles (C)	antiblock properties
	(nm)	
Ex.IV-(25)	20	good
Ex.IV-(26)	80	excellent
C.Ex.IV-(10)	10	poor
C.Ex.IV-(11)	130	excellent

Ex.: Example C.Ex.: Comparative Example

As is obvious from the results shown in Table 9, the polyester film for receiving an ink jet printer image of the present invention is excellent in antiblock properties.

20 Examples IV-(27) and IV-(28) and Comparative Examples IV-(12) and IV-(13)

Biaxially oriented polyester films were obtained in the same manner as in Example IV-(1) except that the ratio of the copolyester (A), the water-soluble polymer (B) and the fine particles (C) was changed as shown in Table 10. The characteristic properties of the obtained laminate films are shown in Table 10.

15

25

Table 10

	(A) copolye	lyester	(B) water-so	ster (B) water-soluble polymer	(C) fine particles	particles	friction coefficient
	type	wt%	type	wts	type	wt&	(st)
Ex.IV-(27)	Ħ	72	Ъ	16	M	3	0.39
Ex. IV-(28)	H	55	P	16	M	20	0.3
C.Ex.IV-(12)	Н	74	Ъ	16	M	П	0.62
C.Ex.IV-(13)	H	48	P	16	Σ	27	0.31

C.Ex.: Comparative Example

Ex.: Example

10

15

20

25

30

As is obvious from the results shown in Table 10, the polyester film for receiving an ink jet printer image of the present invention is excellent in transportability. Example IV-(29)

A composition consisting of 90 wt% of a polyester (intrinsic viscosity of 0.62) composed of a terephthalic acid component and an ethylene glycol component and 10 wt% of titanium oxide was melt extruded onto a rotary cooling drum maintained at 20°C to obtain an unstretched film which was then stretched to 3.6 times in a mechanical axis direction and coated with an aqueous solution composed of 65 wt% of a copolyester (Tq = 30°C, to be simply referred to as "E" hereinafter)) consisting of terephthalic acid (60 mol%), isophthalic acid (36 mol%) and 5-Na sulfoisophthalic acid (4 mol%) as acid components and ethylene glycol (60 mol%) and neopentyl glycol (40 mol%) as glycol components, 16 wt% of a polyvinyl alcohol having a saponification degree of 86 to 89 mol%, 10 wt% of crosslinked acrylic resin particles having an average particle diameter of 40 nm and 9 wt% of polyoxyethylene lauryl ether, and having a solid content of 4 wt% by a roll coater.

The longitudinally stretched film coated with the aqueous solution was stretched to 4 times in a transverse direction while it was dried, and then heat set at 230°C to obtain a 100 µm thick biaxially oriented film. The film had a coating film thickness of 0.03 µm, a center line average surface roughness of 59 nm, a glossiness of 65, a light transmittance of 3 % and a thermal shrinkage factor in a longitudinal direction of 0.9 % and in a transverse direction of 0.2 % and was excellent in sharpness and adhesion.

Comparative Example IV-(14)

A biaxially oriented polyester film was obtained in the same manner as in Example IV-(29) except that the copolyester (A) of Example IV-(29) was changed to L. This film had a

coating film thickness of 0.03 μ m, a center line average surface roughness of 120 nm, a glossiness of 41, a light transmittance of 3 % and a thermal shrinkage factor in a longitudinal direction of 0.9 % and in a transverse direction of 0.2 % and was unsatisfactory in terms of sharpness and adhesion.

Example V-(1)

5

10

15

20

25

30

A polyester (intrinsic viscosity of 0.62) composed of a terephthalic acid component and an ethylene glycol component was melt extruded onto a rotary cooling drum maintained at 20°C to obtain an unstretched film which was then stretched to 3.6 times in a mechanical axis direction and coated with an aqueous solution composed of 51 wt% of a copolyester i.e., the copolyester (A), (Tg = 40°C, to be simply referred to as "E" hereinafter)) which consisted of terephthalic acid (60 mol%), isophthalic acid (36 mol%) and 5-Na sulfoisophthalic acid (4 mol%) as acid components and ethylene glycol(70 mol%) and neopentyl glycol (30 mol%) as glycol components, 20 wt% of a polyvinyl alcohol having a saponification degree of 86 to 89 mol%, 10 wt% of crosslinked acrylic resin particles having an average particle diameter of 40 nm, 10 wt% of a compound (Y) represented by the following formula (II) and 9 wt% of polyoxyethylene lauryl ether, and having a solid content of 4 wt% by a roll coater. longitudinally stretched film coated with the aqueous solution was stretched to 4 times in a transverse direction while it was dried, and then heat set at 230°C to obtain a 100 µm thick biaxially oriented film. The film had a coating film thickness of 0.03 µm, a center line average surface roughness of 15 nm, a surface energy of 61 mN/m and a thermal shrinkage factor in a longitudinal direction of 0.9 % and in a transverse direction of 0.2 %. The characteristic properties of this film are shown in Table 11.

(II)

10

15

Comparative Example V-(1)

The characteristic properties of a biaxially oriented polyester film obtained in the same manner as in Example V-(1) except that the aqueous solution was not coated are shown in Table 11.

Examples V-(2) to V-(10)

Biaxially oriented polyester films were obtained in the same manner as in Example V-(1) except that the composition of the coating film layer was changed as shown in Table 11. The characteristic properties of the obtained laminate films are shown in Table 11.

Table 11

ė,	>-		<u>-</u> -	T	<u>-</u>						.,					
surface	energy				61	57	09	56	63	64	64	58		2/	59	45
sion	after	printing			Ą	Ą	A	A	A	A	A	A		A	A	
adhesion	before	printing			А	A	A	Ą	Ą	K	A		G	Ą	Ą	ပ
	inking	ı	wt%		10	10	10	10	10	10	10	10	0.7	10	10	
yer	(D) crosslinking	agent	type	(note 4)	×	Y	X	H	X	*	\	1 >	Ŧ	Z	Ā	
ilm la	ine	les	wt%		10	10	10	10	10	10	10	2 5	OT	10	7	
on of coating film layer	(C) fine	particles	type	(note 3)	Σ	X	Æ	×	∑	: ≥		E .	Σ	M	z	1
n of c	ter-	polymer	wt%		20	20	20	2.0	20	20	0 0	707	20	20	20	
compositio	(B) water-	soluble p	type	(note 2)	<u>a</u>	d	0	2	: E	- L		S :	×	д	Ъ	1
נ		ster	wt%		51	5 12	5	51	7 L	7 4	ם ב	TC	51	51	54	
	(A)	copolvester	type	(note 1)) H	1 =	1 1	1 -		1 F	H 1	K-1	E-1	R-1	1 1	1
					Ex. V-(1)	Ex V=(2)	Fx V-(3)	For V_(4)	Ter (1 (E)	(C) - X (D)	(0)-X-X-	EX.V-(/)	Ex.V-(8)	Ex.V-(9)	Ex V-(10)	C. Ex. V-(1)

Ex.: Example C.Ex.: Comparative Example

As is obvious from the results shown in Table 11, the polyester film for receiving an ink jet printer image of the present invention is excellent in adhesion.

In Table 11, Table 12 and Table 14, the type (Note 1)

of copolyester (A) denoted by E-1 is the following compound.

E-1: copolyester (Tg = 40°) consisting of terephthalic acid

(60 mol%), isophthalic acid (36 mol%) and 5-Na

sulfoisophthalic acid (4 mol%)/ethylene glycol (70 mol%) and

neopentyl glycol (30 mol%)

In Table 11, Table 12 and Table 14, the types (Note 2) of water-soluble polymer (B) denoted by P, Q, R, T, U, W and X are the following compounds.

P: polyvinyl alcohol having a saponification degree of 86 to 89 mol%

Q: polyvinyl alcohol having a saponification degree of 76 to 82 mol*

R: polyvinyl alcohol having a saponification degree of 91 to 94 mol%

T: polyvinylpyrrolidone having a K value of 26 to 23 and an average molecular weight of 40,000

U: polyvinylpyrrolidone having a K value of 90 to 100 and an average molecular weight of 1,200,000

W: cation modified polyvinyl alcohol having a saponification degree of 74 to 80 mol%

25 X: cation modified polyvinyl alcohol having a saponification degree of 86 to 91 mol%

In Table 11, Table 12 and Table 14, the types (Note 3) of fine particles (C) denoted by M and N are the following compounds.

30 M: crosslinked acrylic particles having an average particle diameter of 40 nm

N: colloidal silica particles having an average particle diameter of 80 nm

In Table 11, Table 12 and Table 14, the types (Note 4)

of crosslinking agent (D) denoted by Y and Z are compounds represented by the following formulas (II) and (III).

$$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\ \text{N-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \text{CH}_2-\text{CH}-\text{CH}_2 \\ \end{array}$$

Examples V-(11) to V-(14) and Comparative Examples V-(2) to V-(5)

Biaxially oriented polyester films were obtained in the same manner as in Example V-(1) except that the ratio of the copolyester (A), water-soluble polymer (B), fine particles (C) and crosslinking agent (D) was changed as shown in Table 12. The characteristic properties of the obtained laminate films are shown in Table 12.

Table 12

composition of coating film layer	(A) copolyester (B) water-soluble polymer (C) fine particles (D) crosslinking agent	type wts type wts type wts type wts		E-1 41 P 30 M 10 Y 10	E-1 60 P 11 M 10 Y 10	E-1 46 P 20 M 10 Y 15	E-1 54 P 20 M 10 Y 7	E-1 21 P 50 M 10 Y 10	E-1 64 P 7 M 10 Y 10	E-1 61 P 20 M 10 Y 0	E-1 31 P 20 M 10 Y 30
	(A) copolyes	type wt	(note 1)								E-1
		1		Ex.V-(11)	Ex.V-(12)	Ex.V-(13)	Ex.V-(14)	C.Ex.V-(2)	C.Ex.V-(3)	C.Ex.V-(4)	C.Ex.V-(5)

printing

Ex.: Example C.Ex.: Comparative Example

As is obvious from the results shown in Table 12, the polyester film for receiving an ink jet printer image of the present invention is excellent in adhesion and transportability.

5 Examples V-(15) and V-(16) and Comparative Examples V-(6) and V-(7)

Biaxially oriented polyester films were obtained in the same manner as in Example V-(1) except that the particle diameter of the fine particles (C) was changed as shown in Table 13. The characteristic properties of the obtained films are shown in Table 13.

Table 13

	average particle diameter of	antiblock
	fine particles (C) (nm)	properties
Ex.V-(15)	20	good
Ex.V-(16)	80	excellent
C.Ex.V-(6)	10	poor
C.Ex.V-(7)	130	excellent

Ex.: Example C.Ex.: Comparative Example

As is obvious from the results shown in Table 13, the polyester film for receiving an ink jet printer image of the present invention is excellent in antiblock properties.

Examples V-(17) and V-(18) and Comparative Examples V-(8) and V-(9)

Biaxially oriented polyester films were obtained in the same manner as in Example V-(1) except that the ratio of the aqueous binder (A), water-soluble polymer (B), fine particles (C) and crosslinking agent (D) was changed as shown in Table 14. The characteristic properties of the obtained laminate films are shown in Table 14.

15

20

25

Pable 14

rriction	coefficient	(kg)			0.38	2,	770	89	3	0.30	
ILIC		-			0	_	·	_	5	0	
	linking	nt	wt%		10	7	nΤ	7	OT	10	
ا د	o (a)	agent	type	(note 4)	×		X	•	I	X	
lm laye	ine	cles	wt%		ო		20	•	-	27	
ating fi	(C) fine	particles	type	(note 3)	M		×	7 4	IXI	M	
on of co	-soluble	mer	wt%		20		20		70	20) I
composition of coating film layer	yester (B) water-soluble		type	(note 2)	Ω	4	Д.		Д	Q	7
U	este	1	wt%		S.R.	2	41	•	09	3.4	!
	(A) copoly		type	(note 1)	7 1	T _ 3	[±	-	Ϋ́	1 1	-
					Ex. V. (17)	(/⊤)_^.¥⊒	Fy V-(18)	(27)	ر 8)-\\	(0) 12-12-12	(で)-/・と

Ex.: Example C.Ex.: Comparative Example

10

15

20

25

30

As is obvious from the results shown in Table 14, the polyester film for receiving an ink jet printer image of the present invention is excellent in transportability. Example V-(19)

A composition consisting of 90 wt% of a polyester (intrinsic viscosity of 0.62) composed of a terephthalic acid component and an ethylene glycol component and 10 wt% of titanium oxide was melt extruded onto a rotary cooling drum maintained at 20°C to obtain an unstretched film which was then stretched to 3.6 times in a mechanical axis direction and coated with an aqueous solution composed of 51 wt% of a copolyester, i.e., the copolyester (A), (Tg = 40°C) which consisted of terephthalic acid (60 mol%), isophthalic acid (36 mol%) and 5-Na sulfoisophthalic acid (4 mol%) as acid components and ethylene glycol (70 mol%) and neopentyl glycol (30 mol%) as glycol components, 20 wt% of a polyvinyl alcohol having a saponification degree of 86 to 89 mol%, 10 wt% of crosslinked acrylic resin particles having an average particle diameter of 40 nm, 10 wt% of a crosslinking agent represented by the following formula (II) and 9 wt% of polyoxyethylene lauryl ether, and having a solid content of 4 wt% by a roll coater. Thereafter, the longitudinally stretched film coated with the aqueous solution was stretched to 4 times in a transverse direction while it was dried and further heat set at 230°C to obtain a 100 µm thick biaxially oriented film. This film had a coating film thickness of 0.03 µm, a center line average surface roughness of 58 nm, a glossiness of 67, a light transmittance of 3 % and a thermal shrinkage factor in a longitudinal direction of 0.9 % and in a transverse direction of 0.2 % and was excellent in sharpness and adhesion.

CLAIMS

- 1. A white biaxially oriented polyester film for use as a base film for receiving an ink jet printer image, which satisfies the following requirements (1) to (4):
- (1) the content of titanium oxide particles having an average particle diameter of 0.1 to 0.5 μm in the polyester film is 5 to 20 wt%;
- (2) the polyester film has an average glossiness of 65 to
 10 95 %;
 - (3) the polyester film has an X-ray diffraction intensity ratio (F-1/F-2) represented by the following formula (1):

$$0.05 \le F - 1/F - 2 \le 0.15 \tag{1}$$

- wherein (F-1) is an X-ray diffraction intensity on a plane (1 $\overline{10}$) parallel to the surface of the film and (F-2) is an X-ray diffraction intensity on a plane (100) parallel to the surface of the film; and
 - (4) the polyester film has a static friction coefficient of 0.3 to 0.6.

20

25

- 2. A white biaxially oriented polyester laminate film for use as a base film for receiving an ink jet printer image wherein a coating film layer substantially made of the following components (A) to (C) is formed on at least one side of the white biaxially oriented polyester film of claim 1;
- (A) 50 to 80 wt% of a copolyester having a secondary transition point of 20 to 90°C;
- (B) 10 to 30 wt% of a water-soluble polymer compound; and(C) 3 to 25 wt% of fine particles having an average particle
 - (C) 3 to 25 wt% of fine particles having an average particle diameter of 20 to 80 nm.
 - 3. The film of claim 1 or 2, wherein the polyester film has a thickness of 50 to 250 μm .

4. The film of claim 1 or 2, wherein the polyester film has a thermal shrinkage factor of 2 % or less when it is kept at 150°C for 30 minutes.

5

5. The film of claim 1 or 2, wherein the polyester film has such whiteness that lightness (L*) and chroma (C*) defined in CIE1976 satisfy the following expressions (1) to (3):

$$L* \ge 90 \tag{1}$$

 $10 C* \ge 3 (2)$

$$2L* + C* \ge 190$$
 (3)

provided that $C^* = \{(a^*)^2 + (b^*)^2\}^{1/2}$.

- 6. The film of claim 1 or 2, wherein the polyester film 15 has an optical density of 0.7 to 1.6.
 - 7. The film of claim 1 or 2, wherein the polyester film has a center line average surface roughness (Ra) of 30 to 100 nm.

- 8. The film of claim 1 or 2, wherein the polyester film has a molecular orientation rate (MOR) of 1.1 to 4.0.
- 9. The film of claim 1 or 2, wherein the polyester film contains inert particles having an average particle diameter of 0.01 to 5.0 µm other than titanium oxide particles in an amount of 0.01 to 5.0 wt%.
- 10. The film of claim 1 or 2, wherein the polyester film30 is formed from polyethylene terephthalate.
 - 11. The film of claim 1 or 2, wherein the coating film layer has a thickness of 0.02 to 1 μm .

- 12. The laminate film of claim 2, wherein the coating film layer has a surface energy of 50 to 70 mN/m.
- 13. The laminate film of claim 2, wherein the coating film
 5 layer is substantially made of (A) 55 to 75 wt% of a copolyester having a secondary transition point of 20 to 90°C,
 (B) 12 to 25 wt% of a water-soluble polymer and (C) 5 to 20 wt% of fine particles having an average particle diameter of 20 to 80 nm.

15

- 14. The laminate film of claim 2, wherein the copolyester (A) of the coating film layer contains a dicarboxylic acid(s) having a sulfonate group in an amount of 1 to 16 mol% based on the total of all the dicarboxylic acid components forming the copolyester.
- 15. The laminate film of claim 2, wherein the copolyester (A) of the coating film layer has a secondary transition point of 25 to 80°C.

20

16. The laminate film of claim 2, wherein the water-soluble polymer compound (B) of the coating film layer is at least one selected from the group consisting of a polyvinyl alcohol, polyvinyl pyrrolidone and polyethylene glycol.

- 17. The laminate film of claim 2, wherein the fine particles (C) of the coating film layer has an average particle diameter of 25 to 50 nm.
- 30 18. The laminate film of claim 2, wherein the coating film layer is formed by blending a polyfunctional epoxy compound into a composition substantially consisting of the components (A), (B) and (C).

5

10

30

19. A polyester laminate film for use as a base film for receiving an ink jet printer image which consists of a polyester film and a coating film layer formed on at least one side of the polyester film, wherein

the coating film layer is substantially made of (A) 50 to 80 wt% of a copolyester containing a dicarboxylic acid component having a sulfonate group in an amount of 1 to 16 mol% based on the total of all the dicarboxylic acid components forming the copolyester and having a secondary transition point of 20 to 90°C, (B) 10 to 30 wt% of a water-soluble polymer compound and (C) 3 to 25 wt% of fine particles having an average particle diameter of 20 to 80 nm and has a surface energy of 54 to 70 mN/m.

15 20. A polyester laminate film for use as a base film for receiving an ink jet printer image which consists of a polyester film and a coating film layer formed on at least one side of the polyester film, wherein

the coating film layer is substantially made of (A) 30

to 80 wt% of an aqueous binder, (B) 10 to 40 wt% of a
water-soluble polymer, (C) 3 to 25 wt% of fine particles
having an average particle diameter of 20 to 80 nm, and (D)
5 to 20 wt% of a polyfunctional epoxy compound crosslinking
agent as the main ingredients and has a surface energy of
50 to 70 mN/m.

21. The laminate film of claim 20, wherein the polyfunctional epoxy compound crosslinking agent is represented by the following formula:

$$\begin{array}{c} \operatorname{CH_2-CH-CH_2} & \operatorname{CH_2-CH-CH_2} \\ \operatorname{N-R-N} & \operatorname{CH_2-CH-CH_2} \\ \\ \operatorname{CH_2-CH-CH_2} & \operatorname{CH_2-CH-CH_2} \end{array}$$

20

25

30

wherein R is
$$-CH_2$$
 $-CH_2$, $-CH_2$ or $-CH_2$.

5 22. A white polyester laminate film for use as a base film for receiving an ink jet printer image which consists of a polyester film and a coating film layer formed from (A) a copolyester, (B) polyalkylene oxide and (C) fine particles as the main ingredients on at least one side of the polyester film, wherein

the polyester film contains 5 to 20 wt% of titanium oxide having an average particle diameter of 0.1 to 0.2 μ m and 0.01 to 5.0 wt% of inert fine particles having an average particle diameter of 0.01 to 5.0 μ m other than titanium oxide and has an average glossiness of 80.5 to 95 % and a static friction coefficient of 0.30 to 0.50.

23. A white polyester laminate film for use as a base film for receiving an ink jet printer image which consists of a polyester film and a coating film layer formed from (A) a copolyester, (B) polyalkylene oxide and (C) fine particles as the main ingredients on at least one side of the polyester film, wherein

the polyester film contains 5 to 20 wt% of titanium oxide having an average particle diameter of 0.1 to 0.2 μ m and 0.01 to 5.0 wt% of inert fine particles having an average particle diameter of 0.01 to 5.0 μ m other than titanium oxide and has an average glossiness of 65 to 80 % and an X-ray diffraction intensity ratio (F-1/F-2) which satisfies the following expression (1):

$$0.05 \le (F-1/F-2) \le 0.15$$
 (1)

wherein (F-1) is an X-ray diffraction intensity on a plane $(1\overline{1}0)$ parallel to the surface of the film and (F-2) is an X-ray diffraction intensity on a plane (100) parallel to the

surface of the film.

- 24. A base film for receiving an ink jet printer image having an ink image receiving layer on the surface of the coating film layer of the laminate film of claim 2.
 - 25. Use of the laminate film of claim 1 as a base film for receiving an ink jet printer image.
- 10 26. Use of the laminate film of claim 2 as a base film for receiving an ink jet printer image.

ABSTRACT

A white biaxially oriented polyester film for use as a base film for receiving an ink jet printer image and a base film for receiving an ink jet printer image which satisfy the following requirements (1) to (4):

- (1) the content of titanium oxide particles having an average particle diameter of 0.1 to 0.5 μm in the polyester film is 5 to 20 wt%;
- 10 (2) the polyester film has an average glossiness of 65 to 95 %;
 - (3) the polyester film has an X-ray diffraction intensity ratio (F-1/F-2) represented by the following formal (1):

$$0.05 \le F-1/F-2 \le 0.15$$
 (1)

- wherein (F-1) is an X-ray diffraction intensity on a plane $(1\overline{10})$ parallel to the surface of the film and (F-2) is an X-ray diffraction intensity on a plane (100) parallel to the surface of the film; and
- (4) the polyester film has a static friction coefficient of20 0.3 to 0.6.

The base film for receiving an ink jet printer image of the present invention is excellent in adhesion, glossiness, opacifying properties and transportability.

(19) 世界知的所有権機関 国際事務局



(43) 国際公開日 2000年12月7日 (07.12.2000)

PCT

(10) 国際公開番号 WO 00/73081 A1

(51) 国際特許分類?:

B41M 5/00, C09D

201/00, 167/00, B32B 27/36

(21) 国際出願番号:

PCT/JP00/03060

(22) 国際出願日:

2000年5月12日(12.05.2000)

(25) 国際出願の言語:

日本語

(26) 国際公開の言語:

日本語

(30) 優先権データ:

特願平11/153539 特願平11/185184

JP 1999年6月1日(01.06.1999) JP 1999年6月30日(30.06.1999)

特願平11/185185

1999年6月30日(30.06.1999)

(71) 出願人 (米国を除く全ての指定国について): 帝人株 式会社 (TEIJIN LIMITED) [JP/JP]; 〒541-0054 大阪府 大阪市中央区南本町1丁目6番7号 Osaka (JP).

(72) 発明者; および

(75) 発明者/出願人 (米国についてのみ): 吉田哲男

(YOSHIDA, Tetsuo) [JP/JP]. 北澤 諭 (KITAZAWA, Satoshi) [JP/JP]. 西郷 孝 (SAIGO, Takashi) [JP/JP]. 福田雅之 (FUKUDA, Masayuki) [JP/JP]. 矢野真司 (YANO, Shinji) [JP/JP]; 〒229-1105 神奈川県相模原市 小山3丁目37番19号 帝人株式会社 相模原研究セン ター内 Kanagawa (JP).

(74) 代理人: 弁理士 大島正孝(OHSHIMA, Masataka); 〒 160-0004 東京都新宿区四谷四丁目3番地 福屋ビル 大 島特許事務所 Tokyo (JP).

(81) 指定国 (国内): KR, US.

(84) 指定国 (広域): ヨーロッパ特許 (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

添付公開書類:

国際調査報告書

2文字コード及び他の略語については、定期発行される 各PCTガゼットの巻頭に掲載されている「コードと略語 のガイダンスノート」を参照。

(54) Title: POLYESTER FILM FOR INK IMAGE RECEIVING SUBSTRATE AND INK IMAGE RECEIVING SUBSTRATE

(54) 発明の名称: インク受像基材用ポリエステルフィルムおよびインク受像基材

(57) Abstract: A white, biaxially orientated polyester film for an image receiving substrate for use in an ink-jet printer, which satisfies the following requirements (1) to (4): (1) the content of titanium oxide particles having an average particle diameter of 0.1 to 0.5 μ m in said polyester film is 5 to 20 wt %, (2) said polyester film has an average gloss of 65 to 95 %, (3) said polyester film has an X-ray diffraction intensity ratio (F-1/F-2) in the range represented by the formula (1): $0.05 \le F-1/F-2 \le 0.15$ wherein F-1 represents an X-ray diffraction intensity by (110) plane parallel with the surface of the film, and F-2 represents an X-ray diffraction intensity by (100) plane parallel with the face of the film, and (4) said polyester film has a static friction coefficient of 0.3 to 0.6; and an image receiving substrate for use in an ink-jet printer. The image receiving substrate for use in an ink-jet printer is excellent in adhesiveness, gloss, hiding property and conveyability.



Declaration and Power of Attorney for Patent Application

特許出願宣言書

Japanese Language Declaration

私は、下欄に氏名を記載した発する:	明として、以下の通り宣言	As a below named inventor, I hereby declare that:				
私の住所、郵便の宛先および国籍 載したとおりであり、	5は、下攔に氏名に続いて記	My residence, post office address and citizenship are as stated below next to my name,				
名称の発明に関し、請求の範囲に の本来の、最初にして唯一の発明 が下欄に記載されている場合)か して共同の発明者である(複数の る場合)と信じ、	引者である(一人の氏名のみ 3、もしくは本来の、最初に	I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled				
in fait to		POLYESTER FILM FOR USE AS AN INK IMAGE				
•		RECEIVING BASE FILM AND INK IMAGE				
		RECEIVING BASE FILM				
その明細書を (該当するほうに印を付す)		the specification of which (check one)				
ここに添付する。		is attached hereto.				
	日に出願番号	☑ was filed on May 12, 2000 as				
第	号として提出し、	International Application Serial No. PCT/JP00/03060 -				
•	日に補正した。	and was amended on				
(該当する場合)		(if applicable)				
私は、前記のとおり補正したの内容を検討し、理解したことを	請求の範囲を含む前記明細書 ≿陳述する。	I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.				
私は、連邦規則法典第37部第 の審査に所要の情報を開示すべ る。	1章第56条(a)項に従い、本願 <き義務を有することを認め	I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).				

IIVEDIEE DIUIDI

Japanese Language Declaration

私は、合衆国法典第35部第119条、第172条、又は第365条 に基づく下記の外国特許出願又は発明者証出願の外国優先権 利益を主張し、さらに優先権の主張に係わる基礎出願の出願 日前の出願日を有する外国特許出願又は発明者証出願を以下 に明記する: I hereby claim foreign priority benefits under Title 35, United States Code §119, §172 or §365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Driority claimed

Prior foreign applications 先の外国出願

			を に を を を 権 の	eu
No. 11-153539	Japan	01/06/1999 ~	X	
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
(番 号)	(国 名)	(出願の年月日)	باد ا	ÆL
No. 11-185184 -	Japan	30/06/1999 ₆ /	X	<u>'</u>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
(番 号)	(国 名)	(出願の年月日)	ຫຼື	fr L
No. 11-185185 / (Number) (番 号)	Japan /	30/06/1999 ビ	X	□
	(Country)	(Day/Month/Year Filed)	Yes	No
	(国 名)	(出願の年月日)	あり	なし
No. 10-326560	Japan	17/11/1998	Yes	X
(Number)	(Country)	(Day/Month/Year Filed)		No
(番 号)	(国 名)	(出願の年月日)		なし
(Number) (番 号)	(Country) (国 名)	(Day/Month/Year Filed) (出額の年月日)	Yes ອ້າງ	□ No なし

私は、合衆国法典第35部第120条に基づく下記の合衆国特許出願の利益を主張し、本願の請求の範囲各項に記載の主題が合衆国法典第35部第112条第1項に規定の態様で先の合衆国出顧に開示されていない限度において、先の出願の出願日と本願の国内出願日又はPCT国際出願日の間に公表された連邦規則法典第37部第1章第56条(a)項に記載の所要の情報を開示すべき義務を有することを認める。

I hereby claim the benefit of Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose any material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(現 況)	(Status)
(出願番号)	(出願日)	特許済み、保属中、放棄済み)	(patended, pending abandoned)
(Application Serial No.)	(Filing Date)	(現 況)	(Status) (patended, pending abandoned)
(出願番号)	(出顧日)	特許済み、保属中、放棄済み)	

私は、ここに自己の知識に基づいて行った陳述がすべて真実であり、自己の有する情報及び信ずるところに従って行った陳述が真実であると信じ、更に故意に虚偽の陳述等を行った場合、合衆国法典第18部第1001条により、罰金もしくは禁固に処せられるか、又はこれらの刑が併科され、又はかかる故意による虚偽の陳述が本願ないし本願に対して付与される特許の有効性を損なうことがあることを認識して、以上の陳述を行ったことを宣言する。

I hereby declare that all statements made herein of my own knowledge are true; and further that all statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Japanese Language Declaration

委任状: 私は、下記発明者として、以下の代理人をここに 選任し、本願の手続きを遂行すること並びにこれに関する一 切の行為を特許商標局に対して行うことを委任する。 (代理人氏名及び登録番号を明記のこと) POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

I hereby appoint John H. Mion, Reg. No. 18.879; Donald E. Zinn, Reg. No. 19.046; Thomas J. Macpeak, Reg. No. 19.292; Robert J. Seas, Jr., Reg. No. 21,092; Darryl Mexic, Reg. No. 23,063; Robert V. Sloan, Reg. No. 22,775; Peter D. Olexy, Reg. No. 24,513; J. Frank Osha, Reg. No. 24,625; Waddell A. Biggart, Reg. No. 24,861; Robert G. McMorrow, Reg. No. 19,093; Louis Gubinsky, Reg. No. 24,835; Neil B. Siegel, Reg. No. 25,200; David J. Cushing, Reg. No. 28,703; John R. Inge, Reg. No. 26,916; Joseph J. Ruch, Jr., Reg. No. 26,577; Sheldon I. Landsman, Reg. No. 25,430; Richard C. Turner, Reg. No. 29,710; Howard L. Bernstein, Reg. No. 25,665; Alan J. Kasper, Reg. No. 25,426; Kenneth J. Burchfiel, Reg. No. 31,333; Gordon Kit, Reg. No. 30,764; Susan J. Mack, Reg. No. 30,951; Frank L. Bernstein, Reg. No. 31,484; Mark Boland, Reg. No. 32,197; William H. Mandir, Reg. No. 32,156; Scott M. Daniels, Reg. No. 32,562; Brian W. Hannon, Reg. No. 32,778; Abraham J. Rosner, Reg. No. 33,276; Bruce E. Kramer, Reg. No. 33,725; Paul F. Neils, Reg. No. 33,102; and Brett S. Sylvester, Reg. No. 32,765, my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and request that all correspondence about the application be addressed to SUGHRUE, MION, Zinn, MACPEAK & SEAS, PLLC, 2100 Pennsylvania Avenue, N.W., Washington, D.C. 20037-3202.

書類の送付先:

Send Correspondence to:

SUGHRUE, MION, ZINN, MACPEAK & SEAS 2100 Pennsylvania Avenue, N.W., Washington, D.C. 20037

直通電話連絡先:

(名称及び電話番号)

Direct Telephone Calls to: (name and telephone number)

(202)293-7060

惟一の又は第一の発明者の氏名		Full name of sole or first inventor
•	1-00	Tetsuo YOSHIDA
司発明者の署名	日付	Inventor's signature Date
· · · · · · · · · · · · · · · · · · ·		Tetro Joshida January 17, 2001
生所		Residence
(Sagamihara-shi, KANAGAWA, JAPAN $\supset \!$
国籍 :		Citizenship
	,	Japanese
郵便の宛先		Post office address _C /o Teijin Limited, Sagamihara
		Research Center, 37-19, Oyama 3-chome,
		Sagamihara-shi, KANAGAWA 229-1105 JAPAN
第二の共同発明者の氏名(該当する場合)		Full name of second joint inventor, if any
第二の共同発明者の氏名(該当する場合)	2-00	<u>Satoshi KITAZAWA</u>
第二の共同発明者の氏名(該当する場合) 	<u> </u>	Satoshi KITAZAWA Second inventor's signature Date
*	<u> </u>	Satoshi KITAZAWA Second inventor's signature Date
*	<u> </u>	Satoshi KITAZAWA Second inventor's signature Date
同第二発明者の署名	<u> </u>	Satoshi KITAZAWA Second inventor's signature Satoshi Kitazawa January 17, 2001
同第二発明者の署名	<u> </u>	Satoshi KITAZAWA Second inventor's signature Satoshi Kitazawa January 17, 2001 Residence
同第二発明者の署名 住所	<u> </u>	Satoshi KITAZAWA Second inventor's signature Satoshi Kitagawa January 17, 2001 Residence Sagamihara-shi, KANAGAWA, JAPAN FR.
同第二発明者の署名 住所	<u> </u>	Satoshi KITAZAWA Second inventor's signature Satoshi Kitazawa January 17, 2001 Residence Sagamihara-shi, KANAGAWA, JAPAN JAPAN Citizenship
同第二発明者の署名 住所 国籍	<u> </u>	Satoshi KITAZAWA Second inventor's signature Satoshi Kitazawa January 17, 2001 Residence Sagamihara-shi, KANAGAWA, JAPAN JAPAN Cittzenship Japanese
同第二発明者の署名 住所 国籍	ジー のひ 日付	Satoshi KITAZAWA Second inventor's signature Satoshi Kitazawa January 17, 2001 Residence Sagamihara-shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara

(第三又はそれ以降の共同発明者に対しても同様な情報 および署名を提供すること。) (Supply similar information and signature for third and subsequent joint inventors.)

第三の共同発明者の氏名 (該当する場合)	_	Full name of third joint inventor, if any
	3-00	Takashi SAIGO
司第三発明者の署名	日付	Takashi SAIGO Third inventor's signature Date
		Takashi Saigo January 17, 2001 Residence
住所		Residence
		Sagamihara-shi, KANAGAWA, JAPAN J
国籍		Citizenship
		Japanese/
郵便の宛先		Post office address c/o Teijin Limited, Sagamihara
		Research Center, 37-19, Oyama 3-chome,
		Sagamihara-shi, KANAGAWA 229-1105 JAPAN
作用のサラックスを (オット・フリム)		Full name of fourth joint inventor, if any
第四の共同発明者の氏名(該当する場合)	11-50	·
C * m * · · · · · · · · · · · · · · · · ·	<u> </u>	Masayuki FUKUDA Fourth inventor's signature Date
同第四発明者の署名	H IJ	
(+ T		Menaguhi Eukuda January 17, 2001
住所		
TER SEE		Sagamihara-shi, KANAGAWA, JAPAN
国籍		·
W III O of the		Japanese Post office address - / - Maiiin Limited Committee
郵便の宛先		Post office address c/o Teijin Limited, Sagamihara Research Center, 37-19, Oyama 3-chome,
		Sagamihara-shi, KANAGAWA 229-1105 JAPAN
第五の共同発明者の氏名(該当する場合)		Full name of fifth joint inventor, if any
İ		
	5-00	Shinji YANO
同第五発明者の署名	5 -00 目付	Fifth inventor's signature Date
	5-00 B付	Fifth inventor's signature Date Shini Vano January 17, 2001
	<u> </u>	Fifth inventor's signature Date Shini Yano January 17, 2001 Residence
同第五発明者の署名	<u> </u>	Fifth inventor's signature Date January 17, 2001 Residence Sagamihara-shi, KANAGAWA, JAPAN
同第五発明者の署名	<u> </u>	Fifth inventor's signature Date Shini Yano January 17, 2001 Residence
同第五発明者の署名 住所 国籍	5 -00 目付	Fifth inventor's signature Date Jhring Jano January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Cittzenship Japanese
同第五発明者の署名 住所	<u>5</u> - <i>0</i> 0	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara
同第五発明者の署名 住所 国籍	<u> </u>	Fifth inventor's signature Date Jhring Jano January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Cittzenship Japanese
同第五発明者の署名 住所 国籍	5 -00 目付	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara
同第五発明者の署名 住所 国籍 郵便の宛先	5 一 <i>〇</i> 〇	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara Research Center, 37–19, Oyama 3-chome, Sagamihara—shi, KANAGAWA 229–1105 JAPAN
同第五発明者の署名 住所 国籍	5 一〇〇 目付	Fifth inventor's signature January 17, 2001 Residence Sagamihara-shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara Research Center, 37-19, Oyama 3-chome,
同第五発明者の署名 住所 国籍 郵便の宛先	日付日付	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara Research Center, 37–19, Oyama 3-chome, Sagamihara—shi, KANAGAWA 229–1105 JAPAN
同第五発明者の署名 住所 郵便の宛先 第六の共同発明者の氏名(該当する場合) 同第六発明者の署名	日付日付	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara Research Center, 37–19, Oyama 3-chome, Sagamihara—shi, KANAGAWA 229–1105 JAPAN Full name of sixth joint inventor, if any Sixth inventor's signature Date
同第五発明者の署名 住所 国籍 郵便の宛先 第六の共同発明者の氏名(該当する場合)	日付日付	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara Research Center, 37–19, Oyama 3-chome, Sagamihara—shi, KANAGAWA 229–1105 JAPAN Full name of sixth joint inventor, if any
同第五発明者の署名 住所 郵便の宛先 第六の共同発明者の氏名(該当する場合) 同第六発明者の署名	日付日付	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara Research Center, 37–19, Oyama 3-chome, Sagamihara—shi, KANAGAWA 229–1105 JAPAN Full name of sixth joint inventor, if any Sixth inventor's signature Date
同第五発明者の署名 住所 国籍 郵便の宛先 第六の共同発明者の氏名(該当する場合) 同第六発明者の署名 住所	日付日付	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara Research Center, 37–19, Oyama 3-chome, Sagamihara—shi, KANAGAWA 229–1105 JAPAN Full name of sixth joint inventor, if any Sixth inventor's signature Date
同第五発明者の署名 住所 国籍 郵便の宛先 第六の共同発明者の氏名(該当する場合) 同第六発明者の署名 住所	日付日付日付日付日付日付日付日付日付日付日付日付日付日日付日日付日日日日日日日	Fifth inventor's signature January 17, 2001 Residence Sagamihara—shi, KANAGAWA, JAPAN Citizenship Japanese Post office address c/o Teijin Limited, Sagamihara Research Center, 37–19, Oyama 3-chome, Sagamihara—shi, KANAGAWA 229–1105 JAPAN Full name of sixth joint inventor, if any Sixth inventor's signature Date Citizenship